PESTICIDE SURFACE WATER AND SEDIMENT QUALITY REPORT

JUNE 2015 SAMPLING EVENT



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Summary

As part of the South Florida Water Management District's (SFWMD) quarterly ambient monitoring program, unfiltered water and sediment samples were collected June 11 to 18, 2015, and analyzed for over 70 pesticides and/or products of their degradation.

The herbicides 2,4-D, ametryn, atrazine, bentazon, diuron, metolachlor, and metribuzin, along with the insecticide/degradate imidacloprid and atrazine desethyl, were detected in one or more of these surface water samples. No harmful impacts are expected from the detected pesticides.

The herbicide ametryn and insecticides/degradates chlordane, DDD, DDE, DDT, dieldrin, beta endosulfan, and endosulfan sulfate, along with three PCB compounds were found in the sediment at several locations. One DDD, three DDE, and two chlordane compound sediment concentrations were of a magnitude considered to have a harmful effect to freshwater sediment-dwelling organisms or wildlife. No harmful impacts are expected from the other detected pesticides.

The compounds and concentrations found are typical of those expected from an area of intensive historical and contemporary agricultural activity.

Background and Methods

The SFWMD pesticide monitoring network includes sites designated in the Everglades Settlement Agreement, the Lake Okeechobee Protection Act Permit, and the non-Everglades Construction

Project (non-ECP) permit. The canals and marshes depicted in **Figure 1** are protected as Florida Administrative Code (F.A.C.) 62-302 Class III (fishable and swimmable) waters, while Lake Okeechobee is protected as a Class I drinking water supply. Water Conservation Area 1 (WCA-1) and the Everglades National Park are also designated as Outstanding Florida Waters, to which anti-degradation standards apply. Surface water and sediment are sampled quarterly and semiannually, respectively, upstream at each structure identified in the permit or agreement. Sediment samples are collected using a petite Ponar® dredge.

Seventy-four pesticides and degradation products were analyzed in samples from 25 of the network 26 sites (**Figure 1**). The analytes, their respective method detection limits (MDLs), and practical quantitation limits (PQLs) are listed in **Table 1**. All the analytical work is performed by the Florida Department of Environmental Protection (FDEP) Central Laboratory in Tallahassee, Florida. Analytical method details can be found at the following location: http://www.dep.state.fl.us/labs/cgibin/sop/chemsop.asp.

To evaluate the potential impacts on aquatic life, the observed concentration is compared to the appropriate criterion outlined in F.A.C. 62-302.530. If a pesticide compound is not specifically listed, acute and chronic toxicity criterion are calculated as one-third and one-twentieth, respectively, of the amount lethal to 50% of the test organisms in 96 hours, using the lowest technical grade effective concentration 50 (EC₅₀) or lethal concentration 50 (LC₅₀) reported in the summarized literature for the species significant to the indigenous aquatic community (F.A.C. 62-302.200). Each pesticide's description and possible uses and sites of application described herein are taken from Hartley and Kidd (1987). Sediment concentrations are compared to freshwater sediment quality assessment guidelines (MacDonald Environmental Sciences, Ltd., and United States Geological Survey, 2003). A value below the threshold effect concentration (TEC) should not have a harmful effect on sediment-dwelling organisms. Values above the probable effect concentration (PEC) demonstrate that harmful effects to sediment-dwelling organisms are likely to be frequently or always observed. This summary covers surface water and sediment samples collected from June 11 to June 18, 2015.

Results

At least one pesticide was detected in surface water at 22 of the 26 sites (**Table 2**) and in sediment at 17 of the 20 sites (**Table 3**). The non-ECP permit requires sampling at S142 only during discharge or flow events. For this sampling event, no sample was obtained due to the lack of discharge at the time of sample collection. A minor modification of the Lake Okeechobee Water Control Structure Operations Permit (#0174552-010, dated December 18, 2011) eliminated sediment sampling at S65E, S191, and FECSR78. Additionally, sediment sampling was reduced to an annual frequency at S2, S3, and S4 for only ametryn, chlordane, DDD, DDE, and DDT analysis, which was performed during this sampling event. Sediment samples are not collected at S333, S356-334, and TAMBR105, due to no requirement in the respective mandate. All of these compounds have previously been detected in this monitoring program.

The above findings must be considered with the caveat that pesticide concentrations in surface water and sediment may vary significantly in relation to the timing and magnitude of pesticide application,

rainfall events, pumping and other factors, and that this was only one sampling event. The possible acute and chronic toxicity and environmental fate impacts are reported based on the single sampling event and do not take into account previous monitoring data.

Usage and Water Quality Impacts

<u>2,4-D</u>: 2,4-D is a selective systemic herbicide used for the post-emergence control of annual and perennial broad leaf weeds in terrestrial (grassland, established turf, sugarcane, rice, and on non-crop areas) as well as aquatic areas. Environmental fate and toxicity data in **Tables 4 and 5** indicate that 2,4-D (1) has minimum loss from soil by surface adsorption, with a moderate loss by leaching and surface solution; (2) is slightly toxic to mammals and relatively non-toxic to fish; and (3) does not bioaccumulate significantly. The highest 2,4-D concentration in surface water was detected at S4 (0.18 micrograms per liter $[\mu g/L]$) (**Table 2**). Using these criteria, this observed level should not have an acute or chronic effect on fish or aquatic invertebrates. 2,4-D was not detected in the sediment.

Ametryn: Ametryn is a selective terrestrial herbicide registered for use on sugarcane, bananas, pineapple, citrus, corn, and non-crop areas. Most algal effects occur at concentrations greater than (>) 10 micrograms per liter (μ g/L) (Verschueren, 1983). Environmental fate and toxicity data in **Tables 4 and 5** indicate that ametryn (1) is lost from soil relatively easily by leaching, surface adsorption, and in surface solution; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data include a 96-hour LC₅₀ of 14.1 milligrams per liter (mg/L) for goldfish (Hartley and Kidd, 1987). The ametryn surface water concentrations found in this sampling event ranged from 0.014 to 0.043 μ g/L (**Table 2**). Using these criteria, these observed surface water concentrations should not have an acute, detrimental impact on fish or aquatic invertebrates. Ametryn was detected in the sediment at S5A at 19 micrograms per kilogram (μ g/Kg) (**Table 3**). However, no sediment guidelines have been developed for ametryn.

Atrazine: Atrazine is a selective systemic herbicide registered for use on pineapple, sugarcane, corn, rangelands, ornamental turf and lawn grasses, and non-crop areas. Environmental fate and toxicity data in **Tables 4 and 5** indicate that atrazine (1) is easily lost from soil by leaching and in surface solution, with moderate loss from surface adsorption; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data include a 96-hour LC₅₀ of 76 mg/L for carp, 16 mg/L for perch, and 4.3 mg/L for guppies (Hartley and Kidd, 1987). Also, in a flow-through bioassay, the maximum acceptable toxicant concentration (MATC) of atrazine was 90 and 210 μg/L for bluegill and fathead minnow, respectively (Verschueren, 1983). The draft ambient aquatic life water quality criterion identifies a one-hour average concentration that does not exceed 1,500 μg/L more than once every three years on the average (United States Environmental Protection Agency [U.S. EPA], 2003a). The atrazine surface water concentrations found in this sampling event at 17 of the 25 sampling locations, ranged from 0.014 to 0.76 μg/L (**Table 2**). Using these criteria, these observed surface water concentrations should not have an acute or chronic detrimental impact on fish or invertebrates. Atrazine was not detected in the sediment.

Atrazine desethyl (DEA) and atrazine desisopropyl (DIA) are biotic degradation products of atrazine. These degradation products are both persistent and mobile in water; however, DEA is more stable and the dominant initial metabolite. Since DEA and DIA are structurally and toxicologically similar to atrazine, the concentrations of total atrazine residue (atrazine + DEA + DIA) may also be a significant consideration in the surface water environment. The DEA to atrazine ratio (DAR, unitless), on a molar basis, has been suggested as an indicator of nonpoint-source pollution of groundwater (Adams and Thurman, 1991) and as a tracer of groundwater discharge into rivers (Thurman et al., 1992). Goolsby et al., (1997) determined that low DAR values, median <0.1, occur in streams during runoff shortly after application of atrazine. Higher DAR values, median about 0.4, occur later in the year after considerable degradation of atrazine to DEA has occurred in the soil (Goolsby et al., (1997). The low median DAR ratio (e.g. 0.28) at the location where both atrazine and DEA were detected, suggests minimum degradation of atrazine (**Table 6**). However, these general guidelines were developed based on observations in Midwest watersheds in northern temperate climates with different soil and water management regimes as well as higher atrazine water concentrations. Applications to the South Florida environment should be made with caution.

Bentazon: Bentazon is a contact herbicide used for post-emergence control of many annual broad-leaved weeds in beans, peas, rice, and established turf. Environmental fate and toxicity data in **Tables 4 and 5** indicate that bentazon (1) is easily lost from soil by leaching, with moderate loss from surface solution, and minimum loss by surface adsorption; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. The highest detected concentration of $0.27 \,\mu\text{g/L}$ at S6 (**Table 2**), is below any level that would have an acute or chronic detrimental impact on fish or aquatic invertebrates.

Chlordane: Chlordane is a chlorinated hydrocarbon previously used as a contact insecticide. Chlordane consists of 72% and 23% of the stereoisomers alpha and gamma chlordane, respectively (U.S. EPA, 1997). Environmental fate and toxicity data in **Tables 4 and 5** indicate that chlordane (1) is moderately toxic to mammals and highly toxic to fish; and (2) has the potential for significant bioconcentration. Freshwater sediment quality assessment guidelines identified a TEC of 3.2 μg/Kg and PEC of 18 μg/Kg for chlordane. The detected sediment residue at S6 and S5A (29 and 26 μg/Kg, respectively) are at a concentration where harmful effects to sediment-dwelling organisms may be frequently or always observed (**Table 3**). While the use of this compound has been discontinued in recent years, its persistence and tendency to accumulate in sediments makes chlordane a compound of concern. Chlordane was not detected in the surface water.

<u>DDD</u>, <u>DDE</u>, <u>DDT</u>: DDE is an abbreviation of **d**ichloro**d**iphenyldichloroethylene [2, 2-bis (4-chlorophenyl)-1, 1-dichloroethene]. DDE is an environmental dehydrochlorination product of DDT (**d**ichloro**d**iphenyl**t**richloroethane), a popular insecticide for which the U.S. EPA cancelled all uses in 1973. The large volume of DDT used, the persistence of DDT, DDE and another metabolite, DDD (**d**ichloro**d**iphenyl**d**ichloroethane), and the high K_{oc} of these compounds account for the frequent detections in sediments. The large hydrophobicity of these compounds also results in a significant bioconcentration factor (**Table 4**). In sufficient quantities, these residues have reproductive effects in wildlife and carcinogenic effects in many mammals.

The detected DDD sediment concentration at S5A (13 μ g/Kg) and S2 (7.0 μ g/Kg) fall between the TEC (4.9 μ g/Kg) and PEC (28 μ g/Kg) (**Table 3**). These concentration may have the possibility for harmful effects on freshwater sediment-dwelling organisms. The DDD concentration detected at S6 (45 μ g/Kg) (**Table 3**), which exceeds the PEC, frequently or always has the possibility for impacting sediment-dwelling organisms. DDD was not detected in the surface water.

The TEC is $3.2 \mu g/Kg$ and the PEC is $31 \mu g/Kg$ for DDE in freshwater sediments. The concentration of DDE detected at S2, S6 and S5A (**Table 3**) exceeded the PEC and frequently or always has the possibility for impacting sediment-dwelling organisms. DDE was not detected in the surface water.

The only DDT concentrations detected (**Table 3**) that exceeded the TEC ($4.2 \,\mu g/Kg$) was at S6 ($9.4 \,\mu g/Kg$). At this level, there could be a possibility for impacting sediment-dwelling freshwater organisms. No DDT was detected in the surface water.

<u>Dieldrin</u>: Dieldrin is a non-systemic insecticide with all uses canceled in the United States. Environmental fate and toxicity data in **Tables 4 and 5** indicate that dieldrin (1) is highly toxic to mammals and fish; and (2) bioconcentrates significantly due to this compounds hydrophobicity. The high K_{oc} and low water solubility accounts for dieldrin's affinity for sediment. The dieldrin concentration at S6 (0.78 μ g/Kg) (**Table 3**) is less than the TEC (1.9 μ g/Kg) and should not have an impact on sediment-dwelling freshwater organisms. Dieldrin was not detected in the surface water.

<u>Diuron</u>: Diuron is a selective, systemic terrestrial herbicide registered for use on sugarcane, bananas, and citrus. Environmental fate and toxicity data in **Tables 4 and 5** indicate that diuron (1) is easily lost from soil in surface solution, with moderate loss from leaching or surface adsorption; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data include a 96-hour LC₅₀ of 25 mg/L for guppies (Hartley and Kidd, 1987). Crustaceans are affected at lower concentrations with a 48-hour LC₅₀ of 1.4 mg/L for water fleas and a 96-hour LC₅₀ of 0.7 mg/L for water shrimp (Verschueren, 1983). Most algal effects occur at concentrations > 10 μg/L (Verschueren, 1983). The highest surface water concentration of diuron found during this sampling event was 0.0063 μg/L at S191 (**Table 2**). Using these criteria, this concentration should not have an acute, harmful impact on fish, aquatic invertebrates, or algae.

Endosulfan: Endosulfan is a non-systemic insecticide and acaricide registered for use on many crops, including beans, tomatoes, corn, cabbage, citrus, and ornamental plants. Technical endosulfan is a mixture of the two stereoisomeric forms, alpha (α) and beta (β). Endosulfan is highly toxic to mammals, with an acute oral LD₅₀ for rats of 70 mg/Kg (**Table 4**). The Soil Conservation Service (SCS) rates endosulfan with an extra small potential for loss due to leaching, a large potential for loss due to surface adsorption and a moderate potential for loss in surface solution (**Table 4**). Beta endosulfan's water solubility and Henry's law constant (1.91 x 10^{-5} atm – m^3 /mole) (Lyman, et al., 1990) indicate volatilization may be significant in shallow waters. The bioconcentration factors indicate a low to moderate degree of accumulation in aquatic organisms (**Table 4**). Beta endosulfan was detected in the sediment at S177 (0.33 µg/Kg) in the South

Miami-Dade County farming area (**Table 3**). However, a sediment quality assessment guideline has not been developed. Endosulfan was not detected in the surface water.

Endosulfan sulfate: Endosulfan sulfate is an oxidation metabolite of the insecticide endosulfan. The water solubility and Henry's law constant (9.63 x 10-8 atm – m3/mole) (Lyman, et al., 1990) indicate that endosulfan sulfate is less volatile than water and concentrations will increase as water evaporates (**Table 4**). Endosulfan sulfate has a relatively high degree of accumulation in aquatic organisms (**Table 4**). Endosulfan sulfate was detected in the sediment at S178 (0.72 μg/Kg) (**Table 3**). However, no sediment quality assessment guideline has been developed for endosulfan sulfate. Endosulfan sulfate was not detected in the surface water.

<u>Imidacloprid</u>: Imidacloprid is a systemic insecticide registered for use on a variety of row crops and turf grass applications as well as for flea control. Environmental fate and toxicity data in **Tables 4** and 5 indicate that imidacloprid (1) is soluble in water; (2) is slightly toxic to mammals and relatively non-toxic to fish; and (3) does not bioconcentrate significantly. The highest detected concentration of $0.11 \, \mu g/L$ at S178 (**Table 2**) is below any level that would have an acute or chronic detrimental impact on fish or aquatic invertebrates.

Metolachlor: Metolachlor is a selective herbicide used on potatoes, sugarcane, and some vegetables. Environmental fate and toxicity data in **Tables 4 and 5** indicate that metolachlor (1) has a large potential for loss due to leaching and a medium potential for loss in surface solution and due to surface adsorption; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Metolachlor is non-toxic to birds (Lyman et al., 1990). The only surface water concentration found in this sampling event $(0.11 \,\mu\text{g/L})$ at S6) (**Table 2**) is orders of magnitude below the calculated chronic toxicity level. Using these criteria, this observed level should not have a harmful effect on fish or aquatic invertebrates. Metolachlor was not detected in the sediment.

Metribuzin: Metribuzin is a selective systemic herbicide used on a variety of crops including potatoes, tomatoes, sugarcane, and peas. Environmental fate and toxicity data in **Tables 4 and 5** indicate that metribuzin (1) has a large potential for loss due to leaching, a medium potential for loss in surface solution, and a small potential for loss due to surface adsorption; (2) is relatively non-toxic to mammals and fish; and (3) does not bioaccumulate significantly. The only concentration of metribuzin detected was $0.11 \mu g/L$ at S6 (**Table 2**). Using these criteria, this surface water concentration should not have an acute impact on fish or aquatic invertebrates. Metribuzin was not detected in the sediment.

<u>PCBs</u>: Polychlorinated biphenyls (PCBs) is the generic term for a group of 209 congeners that contain a varying number of substituted chlorine atoms on one or both of the biphenyl rings. PCB-1248, PCB-1254, and PCB-1260 is a commercial grade mixture containing 48, 54, and 60, respectively, percent chlorine by weight. Production of PCBs was banned in 1978 and closed system uses are being phased out. In natural water systems, PCBs are found primarily absorbed to suspended sediments due to the very low solubility in water (Callahan et al., 1979). The tendency of PCBs for adsorption increases with the degree of chlorination and with the organic content of the

adsorbent. While the production ban, phase out of uses, and stringent spill clean-up requirements have significantly reduced environmental loadings in recent years, the persistence and tendency to accumulate in sediment and bioaccumulate in fish, make this class of organochlorine compounds especially problematic. The TEC and PEC are 60 μ g/Kg and 680 μ g/Kg, respectively, for total PCBs. The sediment residue detected at S6 (120 μ g/Kg) could have an impact freshwater sediment-dwelling organisms. None of the PCB congeners were detected in the surface water.

Quality Assurance Evaluation

No pesticide analytes were detected in the equipment blanks or field blank performed at S18C, S331, S2, S191, US41-25, S8, and S5A. All of the collected samples were shipped and all bottles were received.

Figure 1. South Florida Water Management District Pesticide Monitoring Network.

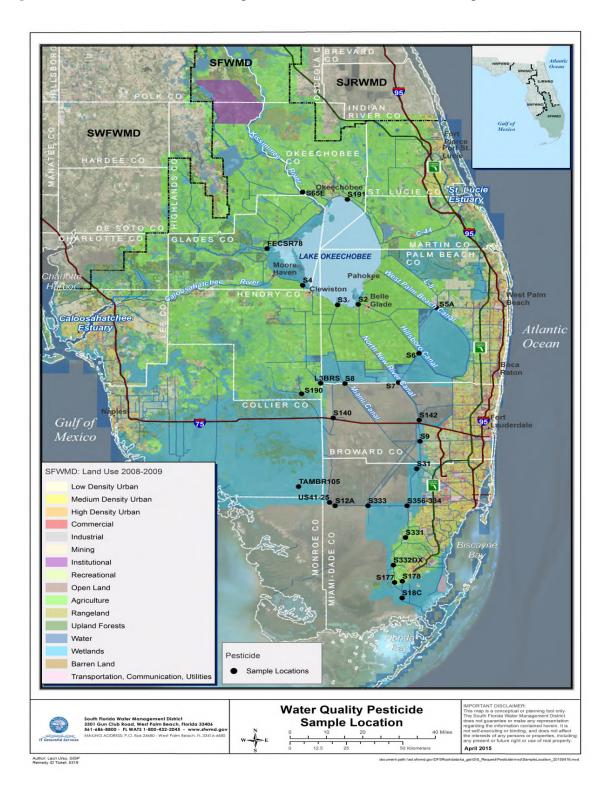


Table 1. Method detection limits (MDLs) and practical quantitation limits (PQLs) for June 2015 sampling event.

event.					
Pesticide or metabolite	Water: range of MDLs - PQLs (µg/L)	Sediment: range of MDLs - PQLs (µg/Kg)	Pesticide or metabolite	Water: range of MDLs - PQLs (µg/L)	Sediment: range of MDLs PQLs (µg/Kg)
2,4-D	0.002 - 0.01	9.1 - 160	endrin aldehyde	0.0037 - 0.016	0.37 - 8.9
2,4,5-T	0.002 - 0.01	9.1 - 160	ethion	0.0094 - 0.04	2.3 - 5.6
2,4,5-TP (silvex)	0.002 - 0.01	9.1 - 160	ethoprop	0.0047 - 0.02	1.2 - 28
acifluorfen	0.002 - 0.01	9.1 - 160	fenamiphos	0.028 - 0.12	0.34 - 110
alachlor	0.056 - 0.06	13 - 400	fonofos	0.0094 - 0.04	1.2 - 28
aldrin	0.0019 - 0.008	0.093 - 2.2	heptachlor	0.0019 - 0.008	0.047 - 1.1
ametryn	0.0094 - 0.04	2.3 - 62	heptachlor epoxide	0.0019 - 0.008	0.093 - 2.2
atrazine	0.0094 - 0.04	2.3 - 56	hexazinone	0.028 - 0.12	7.0 - 170
atrazine desethyl	0.0094 - 0.081	N/A	imidacloprid	0.002 - 0.01	N/A
atrazine desisopropyl	0.0094 - 0.04	N/A	linuron	0.004 - 0.02	1.4 - 33
azinphos methyl (guthion)	0.019 - 0.08	7 - 170	malathion	0.0094 - 0.04	2.3 - 56
bentazon	0.002 - 0.01	N/A	metalaxyl	0.037 - 0.16	N/A
α-BHC (alpha)	0.0019 - 0.008	0.047 - 1.1	methamidophos	N/A	4.2 - 220
β-BHC (beta)	0.0019 - 0.008	0.047 - 1.1	methoxychlor	0.0094 - 0.04	0.047 - 1.1
δ-BHC (delta)	0.0019 - 0.008	0.031 - 0.73	metolachlor	0.056 - 0.24	14 - 330
γ-BHC (gamma) (lindane)	0.0019 - 0.008	0.047 - 1.1	metribuzin	0.019 - 0.08	4.7 - 110
bromacil	0.037 - 0.16	0.34 - 330	mevinphos	0.0094 - 0.04	2.3 - 56
butylate	0.019 - 0.08	N/A	mirex	0.0037 - 0.016	0.093 - 2.2
carbophenothion (trithion)	0.0056 - 0.024	0.14 - 3.3	monocrotophos	N/A	2.8 - 67
chlordane	0.019 - 0.08	0.47 - 12	naled	0.037 - 0.16	9.3 - 220
chlorothalonil	0.0075 - 0.032	0.19 - 4.4	norflurazon	0.028 - 0.12	7.0 - 170
chlorpyrifos ethyl	0.0094 - 0.04	2.3 - 56	parathion ethyl	0.019 - 0.08	2.3 - 56
chlorpyrifos methyl	0.0094 - 0.04	2.3 - 56	parathion methyl	0.0094 - 0.04	2.3 - 56
cypermethrin	0.011 - 0.048	0.23 - 5.6	PCB-1016	0.019 - 0.08	0.93 - 22
DDD-P,P'	0.0037 - 0.016	0.047 - 1.2	PCB-1221	0.019 - 0.08	0.93 - 22
DDE-P,P'	0.0037 - 0.016	0.031 - 3.7	PCB-1232	0.019 - 0.08	0.93 - 22
DDT-P,P'	0.0037 - 0.016	0.11 - 3	PCB-1242	0.019 - 0.08	0.93 - 22
demeton	0.022 - 0.096	2.8 - 67	PCB-1248	0.019 - 0.08	0.93 - 22
diazinon	0.0094 - 0.04	2.3 - 56	PCB-1254	0.019 - 0.08	0.93 - 22
dicofol (kelthane)	0.022 - 0.096	0.093 - 2.2	PCB-1260	0.019 - 0.08	0.93 - 22
dieldrin	0.0019 - 0.008	0.19 - 4.4	permethrin	0.0094 - 0.04	0.11 - 2.7
disulfoton	0.0047 - 0.02	1.2 - 28	phorate	0.0047 - 0.02	1.2 - 28
diuron	0.002 - 0.01	1.4 - 33	prometon	0.019 - 0.08	N/A
α-endosulfan (alpha)	0.0019 - 0.016	0.18 - 100	prometryn	0.019 - 0.08	4.7 - 110
β-endosulfan (beta)	0.0019 - 0.016	0.19 - 34	simazine	0.0094 - 0.04	2.3 - 56
endosulfan sulfate	0.0037 - 0.016	0.093 - 2.2	toxaphene	0.094 - 0.4	4.7 - 110
endrin	0.0037 - 0.016	0.19 - 4.4	trifluralin	0.0075 - 0.032	0.074 - 1.8

N/A = not analyzed

Table 2. Summary of pesticide residues (μ g/L) detected above the method detection limit in surface water samples collected by SFWMD in June 2015.

Date	Location	Flow	2,4-D	ametryn	atrazine	atrazine desethyl	bentazon	diuron	imidacloprid	metolachlor	metribuzin	Number of compounds detected at location	
6/11/2015	S18C	Y	-	-	0.027 I	-	0.044	-	0.014	-	-	3	
	S178	Y	-	-	-	-	0.12	-	0.11	-	-	2	
	S177	N	-	-	0.023 I*	-	0.016 *	-	-	-	-	2	
	S331	N	-	-	0.020 I	0.011 I	0.033	-	-	-	-	3	
	S332DX	N	-	-	0.020 I		0.031	-	-	-	-	2	
6/16/2015	S31	N	0.0037 I	0.014 I	0.043	0.014 I	0.050	-	-	-	-	5	
	S356-334	N	-	-	0.014 I		0.021	-	-	-	-	2	
	S333	N	-	-	-	-	0.0042 I	-	-	-	-	1	
	S12A	N	-	-	-	-	-	-	-	-	-	0	
	US41-25	N	-	-	-		-	-	-	-	-	0	
	TAMBR105	Y	-	-	-	-	-	0.0034 I	-	-	-	1	
6/17/2015	S4	N	0.18	0.031 I	0.40	0.049	0.017	-	0.0022 I	-	-	6	
	S2	N	0.035	-	0.16	0.038	0.0087 I	-	-	-	-	4	
	S3	N	0.039	-	0.14	0.036 I	0.0091 I	-	-	-	-	4	
	S65E	Y	0.019 *	-	0.029 I*	-	0.026 *	-	0.0048 I*	-	-	4	
	S191	N	0.030	-	-	-	0.0043 I	0.0063 I	0.0052 I	-	-	4	
	FECSR78	N	-	-	-	-	-	-	-	-	-	0	
	S140	N	0.036	-	0.024 I	-	0.019	0.0044 I	0.0033 I	-	-	5	
	S190	N	0.0059 I	0.028 I	0.31	0.069	0.091	-	-	-	-	5	
	L3BRS	N	0.041	0.042	0.10		0.11	-	-	-	-	4	
	S8	N	0.043	0.043	0.10	ı	0.10	-	-	-	-	4	
6/18/2015	S6	N	0.14	-	0.76	-	0.27	-	0.0034 I	0.11 I	0.11	6	
	S7	Y	0.017	-	0.048	1	0.12	-	-	-	-	3	
	S5A	Y	0.049	-	0.16	-	0.086	-	-	-	-	3	
	S9	N	0.069	-	-		0.040	-	-	-	-	2	
	Total number of compound detections 14		14	5	17	6	21	3	7	1	1	75	

N = no, Y = yes, R = reverse

^{- =} denotes that the result is below the method detection limit

I = value reported is less than the practical quantitation limit, and greater than or equal to the method detection limit

^{* =} value is the average of replicate samples

Table 3. Summary of pesticides residues ($\mu g/Kg$) detected above the method detection limit in sediment samples collected by SFWMD in June 2015.

Date	Location	Flow	ametryn	chlordane	DDD-P,P'	DDE-P,P'	DDT-P,P'	dieldrin	beta endosulfan	endosulfan sulfate	PCB-1248	PCB-1254	PCB-1260	Number of compounds detected at location
6/11/2015	S18C	Y	-	-	-	1.2 *	-	-	-	-	-	-	-	1
	S178	Y	-	6.0	0.17 I	7.9	-	-	-	0.72 I	-	-	-	4
	S177	N	-	2.8 I	0.97	30	0.60 I	-	0.33 I	-	-	-	-	5
	S332DX	N	-		0.076 I	1.1	-	-	-	-	2.7 I	-	-	3
	S331	N	-	-	0.092 I	1.3	0.78 I	-	-	-	-	ı	-	3
6/16/2015	S31	N	-	-	ı	2.9	-	-	-	-	-	ı	-	1
	S12A	N	-	-	-	0.55	-	-	-	-	-	ı	2.9 I	2
	US41-25	N	-	-	i	0.13 I	-	-	-	-	-	ı	-	1
6/17/2015	S190	N	-	-	ı	0.57	-	-	-	-	-	ı	-	1
	L3BRS	N	-	1.2 I	ı	0.31	-	-	-	-	-	ı	-	2
	S8	N	-	-	-	0.071 I	-	-	-	-	-	-	-	1
	S2	N	-	17	7.0	47	1.1 I	-	-	-	-	-	-	4
	S3	N	-	1.1 I	0.87	2.5	-	-	-	-	-	-	-	3
	S4	N	-	1.2 I*	0.17 I*	1.4 *	-	-	-	-	-	-	-	3
6/18/2015	S7	Y	-	-	-	0.21	-	-	-	-	-	-	-	1
	S6	N	-	29	45	390	9.4	0.78 I	-	-	-	120	-	6
	S5A	Y	19 I	26	13	89	3.2	-	-	-	-	-	-	5
Total nun	nber of comp	ound	1	8	9	17	5	1	1	1	1	1	1	46

N = no, Y = yes, R = reverse

Values in bold, italicized font are at a concentration that harmful effects to sediment-dwelling organisms are likely to be frequently or always observed.

^{- =} denotes that the result is below the method detection limit

I = value reported is less than the practical quantitation limit, and greater than or equal to the method detection limit

^{* =} value is the average of replicate samples

Table 4. Selected properties of pesticides detected during the June 2015 sampling event.

Common Name	Surface Water Standards F.A.C. 62-302	Acute Oral LD ₅₀ For Rats (mg/Kg) (1)	Bioconcentration Factor (2)	Volatility from Water (2)		nservation CS) rating		K _{oc} (mL/g) (3, 4)	Soil Half-life (days) (3, 4)	Water Solubility (WS) (mg/L) (3, 4)	U.S. EPA Carcinogenic Potential (5)
	(µg/L)	(mg Kg) (1)		Water (2)	LE	SA	SS		(day 5) (3, 4)	(Hig E) (3, 4)	1 otentiai (3)
2,4-D (acid)	(100)	375	13	I	M	S	M	20	10	890	D
ametry n	-	1,110	33	I	M	M	M	300	60	185	D
atrazine	-	3,080	86	I	L	M	L	100	60	33	С
bentazon	-	1,100	19	I	L	S	M	34	20	500	С
chlordane	0.0043	365 - 590	3,141	I	-	-	-	3,800	-	0.056	B2
DDD-P,P'	-	3,400	3,173	I	-	-	-	239,900	-	0.055	B2 ⁽⁸⁾
DDE-P,P'	-	880	2,887	S	-	ı	-	243,220	-	0.065	B2 ⁽⁷⁾
DDT-P,P'	0.001	113	15,377	I	-	-	-	140,000	-	0.00335	B2 ⁽⁸⁾
diuron	-	3,400	75	I	M	M	L	480	90	42	D
dieldrin	0.0019	37 - 87	1,873	I	-	-	-	10,000 est.	-	0.14	B2
endosulfan	0.056	70	884	S	XS	L	M	12,400	50	0.53	-
endosulfan sulfate	-	-	2,073	I	-	-	-	-	-	0.117	-
imidacloprid	-	424 ⁽⁶⁾	18	I	-	-	-	178 ⁽⁶⁾	520 ⁽⁶⁾	510 ⁽⁶⁾	Е
metolachlor	-	2,780	18	I	L	M	M	200	90	530	С
metribuzin	-	2,200	11	I	L	S	M	41	30	1,220	D
PCB's	0.014	-	-	-	-	-	-	-	-	-	B2

- = No data available

FDEP F.A.C. 62-302 surface water standards (7/2012) for Class III waters except Class I noted in ()

Bioconcentration Factor (BCF) calculated as BCF = $10^{(2.71-0.564 \log WS)}$ (2); Volatility from water: R = rapid, I = insignificant, S = significant

SCS ratings are pesticide loss due to leaching (LE), surface adsorption (SA) or surface solution (SS) and grouped as large (L), medium (M), small (S), or extra small (XS) B2 = probable human carcinogen; C = possible human carcinogen; D = not classified; E = evidence of non-carcinogen for humans (5)

- (1) Hartley and Kidd (1987)
- (3) Goss and Wauchope (1992)
- (5) U.S. EPA (1996)
- (7) U.S. EPA (1999)

- (2) Lyman, et al. (1990)
- (4) Montgomery (1993)
- (6) U.S. EPA (1994a)
- (8) U.S. Department of Health (1994)

Table 5. Toxicity of pesticides detected during the June 2015 sampling event to freshwater aquatic invertebrates and fishes (μg/L).

	(L		ter Flea nia magna	a)			d Minnow es <i>prome</i>		(Lep		luegill macrochir	us)	Largei (Micropte	mouth Ba			Rainbow Trout [#] (Oncorthynchus mykiss)			Channel Catfish (Ictgalurus punctatus)			
Pesticide Common Name	48 hour I	EC ₅₀	Acute Toxicity (*)	Chronic Toxicity (*)	96 hour I	LC ₅₀	Acute Toxicity	Chronic Toxicity	96 hour L	C ₅₀	Acute Toxicity	Chronic Toxicity	96 hour LC ₅₀	Acute Toxicity	Chronic Toxicity	96 hour L	C ₅₀	Acute Toxicity	Chronic Toxicity	96 hour LC	50	Acute	Chronic Toxicity
2,4-D	25,000	(5)	8,333	1,250	133,000	(5)	44,333	6,650	180,000 900 (48 hr)	(6) (4)	60,000	9,000	-	-	-	100,000 110,000	(2)	33,333 36,667	5,000 5,500	-		-	-
amet ry n	28,000	(5)	9,333	1,400	16,000	(7)	5,333	800	4,100	(2)	1,367	205	-	-	-	8,800	(2)	2,933	440	-		-	-
•				·					·							3,600	(7)	1,200	180				
atrazine	6,900	(5)	2,300	345	15,000	(5)	5,000	750	16,000	(2)	5,333	800	-	-	-	8,800	(2)	2,933	440	7,600	(2) 2	2,533	380
	>100,000	(12)	33,333	5,000					>100,000	(10)	33,333	5,000				5,300	(8)	1,767	265				
bentazon	>100,000	(12)	33,333	5,000	-		-	-	,	(12)	,	5,000	-	-	-	>100,000	(12)	33,333	5,000	-	_	-	-
chlordane	2 200	(4)	1.067	160	4 400	(1)	1 467	- 220	70	(3)	23	3.5	- (1)	- 14	- 2.1	90	(3)	30	4.5	1.500	(1)	-	75
DDD-P,P'	3,200	(4)	1,067	160	4,400	(1)	1,467	220	42	(1)	14	2.1	42 (1)	14	2.1	70	(1)	23	4	-,	(1)	500	75
DDE-P,P'	-		-	-	-	(0)	-	-	240	(1)	80	12	-	-	-	32	(1)	11	2	-	(0)	-	-
DDT-P,P'	-		-	-	19	(3)	6	1	8	(3)	2.7	0.4	2 (3)	0.7	0.1	7	(3)	2	0.4		(3)	5.3	0.8
dieldrin	-		-	-	16	(3)	5.3	0.8	8	(3)	2.7	0.4	-	-	-	10	(3)	3.3	0.5	4.5	(3)	1.5	0.2
diuron	1,400	(5)	467	70	14,200	(5)	4,733	710	5,900	(2)	1,967	295	-	-	-	5,600	(2)	1,867	280	-		-	-
	1,400	(10)	467	70	14,000	(10)	4,667	700	·														
																1	(1)	0.33	0.05				
									1	(1)	0.33	0.05				3	(14)	1.00	0.15	1	(1)	0.33	0.05
endosulfan	166	(5)	55	8	1	(1)	0.33	0.05					-	-	-	1	(13)	0.33	0.05				
									2	(13)	0.67	0.10				0.3	(3)	0.10	0.02	1.5	(5)	0.50	0.08
										()						0.8	(15)	0.27	0.04		` ′		2.00
imidacloprid	85,200	(11)	28,400	4,260	-		-	-	-		-	-	-	-	-	83,000	(11)	27,667	4,150	-		-	-
metolachlor	23,500	(5)	7,833	1,175	-		-	-	15,000	(2)	5,000	750	-	-	-	2,000	(2)	667	100	4,900	(3)	1,633	245
metribuzin	4,200	(5)	1,400	210	_		_	_	80,000	(2)	26,667	4,000		_		64,000	(2)	21,333	3,200	100,000	(5) 3	33,333	5,000
	4,200	(9)	1,400	210					75,900	(9)	25,300	3,795				76,770	(9)	25,590	3,839	,000	(=)	,	2,200

^{- =} No data available

(#) Species is not indigenous. Information is given for comparison purposes only.

(1) Johnson and Finley (1980)

(5) U.S. EPA (1991)

(9) U.S. EPA (1998)

(13) Sneider (1979)

(2) Hartley and Kidd (1987)

(6) Mayer and Ellersieck (1986)

(10) U.S. EPA (2003b)

(14) U.S. EPA (1977)

(3) Montgomery (1993)

(7) U.S. EPA (2005)

(11) U.S. EPA (1994a)

(15) U.S. EPA (2002)

(4) Verschueren (1983)

(8) U.S. EPA (2006)

(12) U.S. EPA (1994b)

^(*) Florida Administrative Code (F.A.C.) 62-302.200, for compounds not specifically listed, acute and chronic toxicity standards are calculated as one-third and one-twentieth, respectively, of the amount lethal to 50% of the test organisms in 96 hours, where the 96 hour LC₅₀ is the lowest value which has been determined for a species significant to the indigenous aquatic community.

Table 6. Atrazine Desethyl (DEA)/Atrazine ratio (DAR) data for June 2015 sampling event.

Doto	Site	Flow*	at	razine	atrazine	desethyl	DAR
Date	Site	LIOW.	μg/L	moles/L	μg/L	moles/L	DAK
6/11/2015	S331	N	0.020	9.27E-11	0.011	5.86E-11	0.63
6/16/2015	S31	N	0.043	1.99E-10	0.014	7.46E-11	0.37
6/17/2015	S 4	N	0.40	1.85E-09	0.049	2.61E-10	0.14
6/17/2015	S2	N	0.16	7.42E-10	0.038	2.03E-10	0.27
6/17/2015	S 3	N	0.14	6.49E-10	0.036	1.92E-10	0.30
6/17/2015	S190	N	0.31	1.44E-09	0.069	3.68E-10	0.26
				DAR	All sites	Flow only sites	No flow sites
				average	0.33	-	0.33
				median	0.28	-	0.28
		minimum	0.14	-	0.14		
				maximum	0.63	-	0.63

^{*} N = no, Y = yes, R = reverse

⁻ no data

Glossary

- Bioconcentration Factor: The ratio of the concentration of a contaminant in an aquatic organism to the concentration in water, after a specified period of exposure via water only. The duration of exposure should be sufficient to achieve a near steady-state condition.
- EC₅₀: A concentration necessary for 50 percent of the aquatic species tested to exhibit a toxic effect short of mortality (e.g., swimming on side or upside down, cessation of swimming) within a short (acute) exposure period, usually 24 to 96 hours.
- Henry's law constant (H): Relates the concentration of a compound in the gas phase to its concentration in the liquid phase. The constant is calculated from the formula: $H = P_{vp}/S$ where P_{vp} is pressure in units of atmospheres and S is solubility in units of moles/meter³ for a compound.
- K_{oc}: The soil/sediment partition or sorption coefficient normalized to the fraction of organic carbon in the soil. This value provides an indication of the chemical's tendency to partition between soil organic carbon and water.
- LC₅₀: A concentration which is lethal to 50 percent of the aquatic animals tested within a short (acute) exposure period, usually 24 to 96 hours.
- LD₅₀: The dosage which is lethal to 50 percent of the terrestrial animals tested within a short (acute) exposure period, usually 24 to 96 hours.
- Method Detection Limits (MDLs): The minimum concentration of an analyte that can be detected with 99 percent confidence of its presence in the sample matrix.
- Practical Quantitation Limits (PQLs): The lowest level of quantitation that can be reliably achieved within specified limit of precision and accuracy during routine laboratory operating conditions. The PQLs are further verified by analyzing spike concentrations whose relative standard deviation in 20 fortified water samples is < 15 percent. In general, PQLs are 2 to 5 times larger than the MDLs.
- Probable Effect Concentration (PEC): The probable effect concentration is intended to identify concentrations above which harmful effects to sediment-dwelling organisms are likely to be frequently or always observed.
- Soil or water half-life: The time required for one-half the concentration of the compound to be lost from the water or soil under the conditions of the test.

Threshold Effect Concentration (TEC): The threshold effect concentration is intended to identify concentrations below which harmful effects to freshwater sediment-dwelling organisms are unlikely to be observed.

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